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A novel model predicting the residence-time distribution during reactive extrusion

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Abstract—A new model for the residence-time distribution in a counter rotating twin-screw extruder is compared with experimental results obtained during the gelatinisation of starch and the grafting of polystyrene on starch. The model consists of a transfer function from which the first three moments can be derived and is based on physical principles without any adjustable parameters. In the model and during experiments, parameters like screw rotation, fully filled length and throughput have been varied. By comparing calculated residence-time distributions with the measurements conclusions about the extruder hold-up and the fully filled extruder length can be drawn. As an extra parameter, the density change of the extruded material was needed to model the residence-time distribution curve during the grafting of polystyrene on starch. © 1997 Elsevier Science Ltd

Keywords: Residence-time distribution; reactive extrusion; starch modifications.

INTRODUCTION

In the past years a growing interest has emerged in using twin screw extruders as chemical reactors both for the polymerisation to and the grafting of synthetic polymers and for the modification of starches. Especially when extruders are used as chemical reactors, a good understanding of mass flow, rheology, mixing time and thermal behaviour is important. Although twin-screw extruders are being used in various industrial applications, this understanding needed for reactor modelling, is still underdeveloped. In this paper we will focus on the modelling and measuring of the mass flows using the residence-time distribution concept.

Residence-time distributions (RTDs) during the processing of synthetic polymers or starches in twin screw extruders have been studied by numerous people. Altomare and Ghossi (1986), Jager *et al.* (1991), Ollet *et al.* (1989), Rauwendaal (1990) and Todd and Irving (1969); reported the results of RTD measurements carried out in a self-wiping twin-screw extruder. Van Zuilichem *et al.* (1988) reported the results of RTD measurements carried out in a conical counter rotating twin screw extruder, Janssen *et al.* (1979), Rauwendaal (1990) and Todd (1975) reported measurements carried out in a parallel counter rotating twin-screw extruder. All models, described in these articles, were based on Newtonian isoviscous fluids

and do not take parameters like density changes into account. This last effect should have some influence on the RTD. For instance measurements done with PVC reveal that at temperatures and pressures commonly found in extrusion processes, density changes of $0.7\text{--}1.4\text{ g cm}^{-3}$ occur (Albers, 1976).

Another interesting problem is the influence of a reaction during extrusion on the residence-time distribution. Parameters like viscosity, material density, temperature and conversions are related to each other and change rapidly during reaction (Ganzeveld and Janssen 1993), so some influence on the RTD could be expected.

A way of bypassing the laborious amounts of measurements describing the viscosity as a function of conversion, temperature and pressure, is by measuring the RTD during the extrusion process. In 1988, Speur did this exercise by studying the RTD during the anionic polymerization of ϵ -caprolactam to Nylon-6. From this study it was concluded that in his case there was no significant difference between the RTD behaviour of a twin-screw extruder with or without reaction. However, his model could not describe all the measurements performed.

In order to be able to predict all residence-time distributions for both reactive and non-reactive extrusion processes, a new model was set-up and tested using gelatinised starch as a test system. In order to examine the effects of reactive extrusion on the residence-time distribution a graft copolymerisation reaction of starch and styrene was performed.

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THEORY

Twin-screw extrusion

Extruders are used in the polymer and food industry. Various types of extruders exist, all with their specific advantages and disadvantages. In twin-screw extruders and especially in the closely intermeshing types, the transport occurs by positive conveying. Because of the intermeshing of the screws the material cannot rotate with the screws, independent of the material properties. The throughput is, within wide limits, independent of back-pressure, viscosity and slip. This is especially important for reactive extrusion where components of largely different viscosities have to be mixed and where considerable viscosity changes may occur.

The counter-rotating twin-screw extruder used in this study is closely intermeshing and therefore consists of series of C-shaped chambers (Figs 1 and 2) in which material is transported from the hopper to the die (Janssen, 1978). This type of extruder has basically three zones; the solids transport zone where solid material is transported and the temperature is raised, the partly filled zone where the chambers are partially empty and starch starts gelatinising, the pump zone where the chambers are completely filled with material and pressure is build up. Between the partially

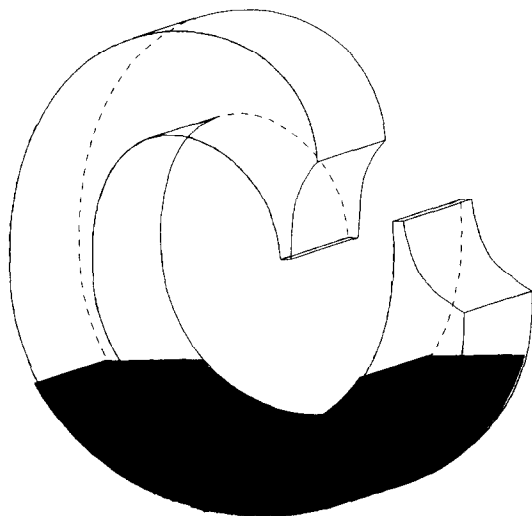


Fig. 1. C-shaped chamber.

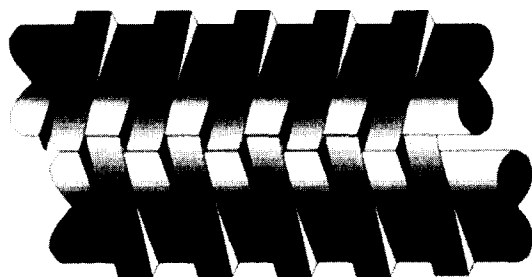


Fig. 2. Series of C-shaped chambers.

filled zone and the fully filled zone a transfer zone exists. In this zone chambers are filled up.

The theoretical throughput of the extruder equals the number of C-shaped chambers transported per unit time multiplied by the chamber volume:

$$Q_{th} = 2mNV_c \quad (1)$$

where N is the screw speed, 2 the number of screws, m the number of thread starts per screw and V_c the volume of a C-shaped chamber.

Between the two screws and between the screws and the barrel surface, mechanical clearances exist. These clearances, where back leakage of material occurs, can be divided into four leakage gaps; the calendar gap, the tetrahedron gap, the side gap and the flight gap. In the fully filled zone the throughput is connected to the leakages through these gaps (Janssen, 1978):

$$Q_{real} = Q_{th} - Q_{leak} \quad (2)$$

where Q_{leak} is the sum of all leakage flows over a cross-section of the extruder.

The leakage flows are driven by inter-chamber pressure differences and conveying of the moving surfaces:

$$Q_f = A_f N + B_f \frac{\Delta p}{\eta}, \quad Q_s = A_s N + B_s \frac{\Delta p}{\eta} \quad (3a)$$

$$Q_t = A_t N + B_t \frac{\Delta p}{\eta}, \quad Q_c = A_c N + B_c \frac{\Delta p}{\eta}$$

here the subscript f, t, s, c stand for tetrahedron, flight, calendar and side gap or, by summation:

$$Q_{leak} = AN + B \frac{\Delta p_i}{\eta_i} \quad (3b)$$

A and B are constants, dependent only on screw and barrel geometry, N is the screw speed, Δp_i is the pressure difference between two consecutive chambers and η_i is the viscosity of the mixture at that position. With this equation, each separate leakage flow can be calculated. The total leakage flow can be described by

$$Q_{leak} = Q_t + 2Q_f + 2m(Q_c + Q_s). \quad (4)$$

Modelling the residence-time distribution

The residence time in an extruder is equal to the filled volume divided by the volumetric throughput. Because the filling degree of the chambers in the partially filled zone can be approximated as $\alpha = Q_{real}/Q_{th}$, the average residence time in an extruder with constant chamber volume can be expressed in its most simple form as:

$$\tau = \frac{V}{Q_{real}} = \frac{((v_t - v_f)(Q_{real}/2mNV_c) + v_f)V_c + V_d}{Q_{real}} \quad (5)$$

where v_f is the amount of filled chambers, v_t is the total amount of chambers, V_c is the chamber volume and V_d the die volume (Pieters, 1993).

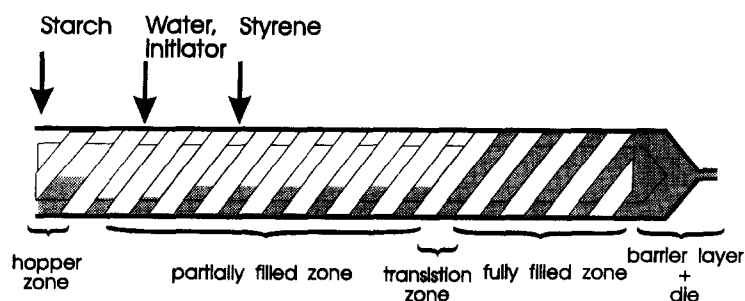


Fig. 3. Extruder zones.

This general equation does not deal with the different leakage flows in an extruder, it only describes the residence time and not the residence-time distribution. A more sophisticated model should be developed. As has been explained before, an extruder can be divided into several zones (Fig. 3). In order to come as close as possible to reality for every zone a different mathematical description is used.

- In the hopper zone, directly below the hopper, where the material is fed to the extruder, the chambers are not yet closed and a considerable back mixing over the flights occurs. This zone can be modelled as one continuously stirred tank.
- In the partially filled zone the chambers are not completely filled with material. Moreover, no pressure gradient is present in this zone and, as a result, the leakages only consist of drag flow.
- In the transition zone the amount of in- and out-flowing material through the leakage gaps is different; resulting in a change in hold-up in the chambers. As has been verified by opening the extruder and visual observation, the amount of chambers in this zones equals 2 times the number of thread starts per screw.
- In the fully filled zone, pressure is build up. If the chamber volume in this zone is constant and the density does not change the total amount of leakage is constant throughout this zone.
- At the end of the screws the material is discharged into the die. In order to account for the effect, that physically no back leakage from the die into the last chambers occurs, a buffer zone is introduced in the model. The concentration of tracer in this zone equals the average concentration in the last four chambers and from this zone a virtual leakage of material into these last four chambers occurs. Especially for small die volumes the influence of the die on the distribution of residence times can be neglected, therefore plug-flow behaviour is assumed in the die.

From these arguments the following assumptions were derived:

- Every C-shaped chamber is assumed to behave as a CST (continuously stirred tank).

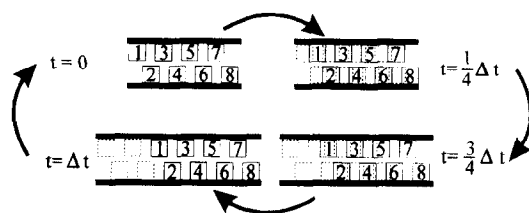


Fig. 4. Moving of C-shaped chambers.

- After one revolution, the content of each chamber is transferred to the next appropriate chamber on the same screw (Fig. 4).
- In the partially filled zone no pressure flow exists in the leakage gaps.
- Plug flow occurs in the die.
- The hopper zone behaves as one CST.
- The density in the partially filled zone is constant but may differ from the constant density in the fully filled zone.
- All density changes occur in the transition zone.

The hopper zone

As stated above, the zone located directly below the hopper is well mixed and modelled as one continuous stirred tank:

$$V_h \frac{dc_h(t)}{dt} = Q_{in}c_0 - Q_{out}c_h(t) \quad (6)$$

in which V_h is the volume of the hopper zone, c_0 and c_h are the input and exit concentrations of the hopper zone. Because the density is constant in this zone both inflow and outflow equal the actual (volumetric) throughput of the extruder: $Q_{in} = Q_{out} = Q$ and $\Delta t \cong 1/N$. This can be rewritten in a finite difference form

$$c_h(t_{n+1}) = \frac{Qc_0(t_n)}{V_h N} + \left(1 - \frac{Q}{V_h N}\right) c_h(t_n) \quad (7)$$

here $n = 0, 1, 2, 3, \dots$ etc. The concentrations in the hopper zone are calculated at the time steps: $t_0 = 0$ s, $t_1 = N^{-1}$ s, $t_{n+1} = (n+1)N^{-1}$ s. At $t = 0$, a pulse is added to the hopper zone so at $t > 0$:

$$c_h(t_{n+1}) = \left(1 - \frac{Q_{in}}{V_h N}\right) c_h(t_{i=n}) \text{ for } n > 0.$$

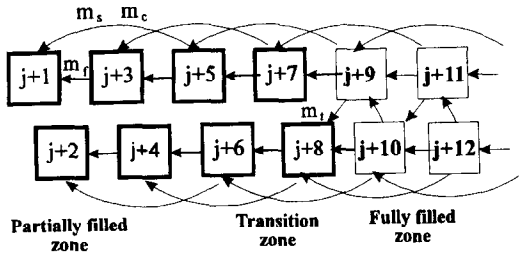


Fig. 5. Mass-flows in a extruder with double thread start screws.

The partially filled zone

From the hopper zone the material is transferred to the partially filled zone. In this zone no pressure gradient is present and therefore the leakage flows only consist of drag components.

For screws with m flights each, the following differential balance over a chamber in this zone can be set up:

$$V_{pf} \frac{dc(j, t)}{dt} = Q_{pf} c(j+2, t) + (Q_{pc} + Q_{ps}) c(j+2m, t) - (Q'_{pc} + Q'_{ps} + Q'_{pf}) c(j, t). \quad (8)$$

In which $c(j+2, t)$ is the concentration of the material coming through the flight gap, Q is the amount of outgoing material and Q' is the amount of incoming material through the leakage gaps. This material originally comes from the chamber situated behind chamber j (Fig. 5). In this figure also the convention for the numbering of the different chambers can be found. The concentration named $c(j+2m, t)$ is material coming through the calander—and the side gap. The difference equation now becomes

$$c(j, t_{i+1}) = \frac{Q_{pf} \Delta t}{V_{pf}} c(j+2, t_i) + \frac{(Q_{pc} + Q_{ps}) \Delta t}{V_{pf}} c(j+2m, t_i) + \left(1 - \frac{(Q'_{pc} + Q'_{ps} + Q'_{pf}) \Delta t}{V_{pf}} \right) c(j, t_i). \quad (9)$$

One screw rotation is divided into μ steps to increase the stability and the precision of the model. One time interval equals: $\Delta t = (1/N)/\mu = 1/(N\mu)$. After one rotation $t_n = t_{i=\mu}$, so the time coordinate can be written as: $t = n + (i/\mu)/N$.

For chambers which are in contact with the hopper zone no back leakage occurs. These chambers are filled during one rotation of a screw by material from the hopper zone and material leaking back from the rest of the partially filled zone. The last term in eq. 9 must be set equal to zero for these particular chambers.

The leakage flows in the rest of the zone are constant because of the constant density (no compressibility effects). As a result, there will be no volume change in the partially filled zone. Because the chambers in the partially filled zone have a larger volume

than needed to transport the material, a degree of fill α has to be defined.

$$Q_{th, pf} = 2\alpha m N V_c$$

$$Q_{leak, pf} = Q_t + 2Q_f + 2m(Q_c + Q_s) = 2\alpha N(A_f + mA_s + mA_c)$$

and

$$Q_{in, pf} = Q_{th, pf} - Q_{leak, pf} \wedge Q_{in, pf} = Q_{in} \Rightarrow$$

$$Q_{in} = 2\alpha N(mV_c - A_f - mA_s - mA_c) \Rightarrow \quad (10)$$

$$\alpha = \frac{Q_{in}}{2N(V_c m - A_f - mA_s - mA_c)}.$$

So

$$V_{pf} = \alpha V_c. \quad (11)$$

Between the partially filled zone and the fully filled zone a transfer zone of $2m$ chambers exists. Due to the pressure acting in the filled zone, material is leaking back into these chambers. As a result these chambers are completely filled after one rotation.

The fully filled zone

In this zone the leakage flows are not only controlled by the screw rotations but also by the pressure gradient. The following differential balance can be set up for a chamber in this zone:

$$V_c \frac{dc(j, t)}{dt} = Q_f c(j+2, t) + Q_t c(j+1, t) + (Q_c + Q_s) c(j+2m, t) - (Q'_c + Q'_t + Q'_s + Q'_f) c(j, t). \quad (12)$$

The difference balance for chambers in this zone equals:

$$c(j, t_{i+1}) = \frac{Q_f \Delta t}{V_c} c(j+2, t_i) + \frac{Q_t \Delta t}{V_c} c(j+1, t_i) + \frac{(Q_c + Q_s) \Delta t}{V_c} c(j+2m, t_i) + \left(1 - \frac{(Q'_c + Q'_s + Q'_f + Q'_t) \Delta t}{V_c} \right) c(j, t_i) \Delta t \quad (13)$$

In reality, the volume of the effective chambers decreases when the material is discharged at the end of the screws. For modelling purposes the volume of these chambers is kept constant and in order to prevent an unrealistic back leakage from the die into the last chambers, a buffer zone is introduced. Such a phenomenon can be imagined as if material, Q_{leak} , is leaking from an infinite thin barrier layer, situated between the die and the screw, back into the last four chambers of the screw. During this leaking no material is transported from the chambers into the die. Because the mass balance has to be consistent, material is flowing after one rotation from the last $2m$ chambers into the die.

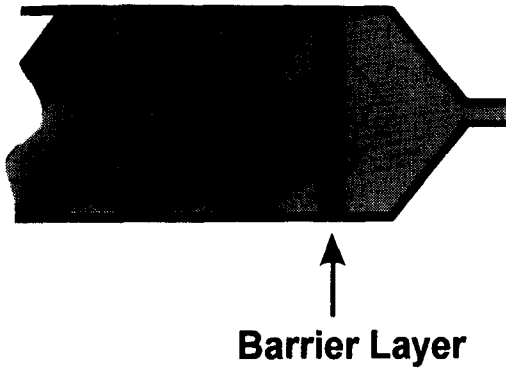


Fig. 6. The (fictive) barrier layer.

The die

As already mentioned above, the die and the screws are separated by a fictive barrier layer (Fig. 6). The differential equation for this layer is:

$$V_{bl} \frac{dc_{bl}(t)}{dt} = Q_{in} c_s(t) - (Q_{leak} + Q_{out}) c_{bl}(t) \quad (14)$$

where c_s is the average concentration of the last four chambers. Material from these chambers is transported through the barrier layer into the die.

Because the change in concentration of the barrier layer is related to the concentration of material entering and leaving the chamber, we used a backwards Euler-method to change the differential equation into the difference equation below:

$$V_{bl} \frac{c_{bl}(t_{n+1}) - c_{bl}(t_n)}{1/N} = 2mV_c N c_s(t_{n+1}) - (Q_{leak} + Q_{in}) c_{bl}(t_{n+1}) \Leftrightarrow \quad (15)$$

$$c_{bl}(t_{n+1}) = \frac{2mV_c}{V_{bl} + 2mV_c} c_s(t_{n+1}) + \frac{V_{bl}}{V_{bl} + 2mV_{bl}} c_{bl}(t_n)$$

where V_{bl} is the volume of the barrier layer, c_{bl} is the concentration in the barrier layer, $c(t_{n+1}) - c(t_n)$ is the change of concentration in the barrier layer during one-screw rotation. The index n keeps track of the number of screw rotations. Because the barrier layer is a hypothetical layer with a zero thickness, it also has a zero volume:

$$\begin{aligned} \lim_{V_{bl} \rightarrow 0} c_{bl}(t_{n+1}) &= \lim_{V_{bl} \rightarrow 0} \left[\frac{2mV_c}{V_{bl} + 2mV_c} c_s(t_{n+1}) + \frac{V_{bl}}{V_{bl} + 2mV_c} c_{bl}(t_n) \right] \\ &\approx \left[\frac{2mV_c}{0 + 2mV_c} c_s(t_{n+1}) + \frac{0}{0 + 2mV_c} c_{bl}(t_n) \right] \\ &= c_s(t_{n+1}). \end{aligned} \quad (16)$$

The concentration in the layer equals the average concentration in the last four chambers of the screw,

so $c_{bl}(t_{n+1}) = c_s(t_{n+1})$. Material that has passed the barrier layer cannot be transported back onto the screws. In this case we assumed that axial mixing can be neglected, compared to the mixing which occurs on the screws. The time necessary for the material to flow through the die is

$$t_d = \frac{V_{die}}{Q_{real}} \quad (17)$$

where V_{die} is the die volume.

The model

The difference equations describing the concentrations on the screws are all of the following structure:

$$c(j, t_{i+1}) = f_i^j \{ c(j, t_i), c(j+1, t_i), c(j+2, t_i), \dots \}. \quad (18)$$

This system of equations can be transformed into a matrix (M) equal to

$$\begin{pmatrix} c_d \\ c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_{bl} \end{pmatrix}_{t_{i+1}} = \begin{pmatrix} 1 & 0 & 0 & 0 & \dots & 0 \\ 0 & 1 & 0 & [Q_f \Delta t / V_h] & \dots & 0 \\ 0 & 0 & 1 & 0 & \dots & 0 \\ 0 & 0 & 0 & [1 - Q_f \Delta t / V_h] & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & 0 & \dots & 1 \end{pmatrix} \begin{pmatrix} c_d \\ c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_{bl} \end{pmatrix}_{t_i} \quad (19)$$

This set of equations can be solved simultaneously during a time step. To obtain a stable mathematical solution, the time necessary for one revolution is divided into μ time steps (Δt) and the concentration distribution after one revolution is:

$$\overline{c(t_{i=\mu})} = (M^\mu) \overline{c(t_{i=0})}. \quad (20)$$

M is the matrix containing all the leakage flow parameters. Both concentrations are in vector notation. After one revolution of the screw all chambers are renumbered. The content of chamber j moves to chamber $j + 2m$ when one rotation has passed. In the time domain this means that $t_{n+1} = t_{i=\mu}$ (the label $n + 1$ is keeping track of the amount of screw rotations, $i = \mu$ is the label that keeps track of the amount of steps during one screw rotation). The matrix M^μ should approach an asymptotic matrix A in which the matrix A equals: $\lim_{m \rightarrow \infty} M^\mu = A$ with $\mu = 1/(N \Delta t)$.

If this is not the case, the time step should be decreased. After one rotation the chambers situated in the hopper zone are becoming chambers in the partially filled zone. Because the volume of a chamber in the hopper zone may differ from the volume in the partially filled zone, the next equation can be set up to

adjust the hopper zone volume to the partially filled volume:

$$\begin{aligned} c(j+2m, t_{n+1}) &= \frac{V_h}{V_{pf}} c(j, t_{i=\mu}) = \frac{Q_{in}/2mN}{\alpha V_c} c(j, t_{i=\mu}) \\ &= \frac{Q_{in}}{2m\alpha V_c N} c(j, t_{i=\mu}). \end{aligned} \quad (21)$$

The transfer chambers are pushed into the fully filled zone during one revolution. This means that their volume changes from partially to fully filled. For these chambers, in which chamber $j+2m$ is a chamber in the fully filled zone and chamber j is the transfer chamber, the following equation can be set up to correct the volume:

$$\begin{aligned} c(j+2m, t_{n+1}) &= \frac{V_{pf}}{V_c} c(j, t_{i=\mu}) = \frac{\alpha V_c}{V_c} c(j, t_{i=\mu}) \\ &= \alpha c(j, t_{i=\mu}). \end{aligned} \quad (22)$$

For the transfer of material coming from the last chambers in the fully filled zone to the boundary layer (c_{bl}) and the die the following equation can be set up:

$$c_{bl}(t_{n+1}) = c_s(t_{n+1}) = c_s(t_{i=\mu}) = \frac{1}{2m} \sum_{2m} \{c_{(v-2m)}(t_{i=\mu})\} \quad (23)$$

here $c_{(v-2m)}$ are the concentrations in the last chambers on the screws. All these equations are of the same form [eq. (24)] and can be transferred into a matrix \mathfrak{R} (25):

$$c(j, t_{n+1}) = f\{c(j_1, t_{i=\mu}), c(j_2, t_{i=\mu}), c(j_3, t_{i=\mu}), \dots\} \quad (24)$$

$$\overline{c(t_{n+1})} = \mathfrak{R} \overline{c(t_{i=\mu})}. \quad (25)$$

Finally, the matrices \mathfrak{R} and M can be put together:

$$\overline{c(t_{i=\mu})} = (M^n) \overline{c(t_n)} \text{ and } \overline{c(t_{n+1})} = \mathfrak{R} \overline{c(t_{i=\mu})}$$

resulting for one revolution in:

$$\overline{c(t_{n+1})} = (\mathfrak{R} \cdot M^n) \overline{c(t_n)}. \quad (26)$$

The concentration in the flow leaving the die is:

$$c(t_n + \tau_{die}) = I(\mathfrak{R} \cdot M^n) \overline{c(t_0)} \text{ with } I = (0 \ 0 \ \dots \ 0 \ 1) \quad (27)$$

in which I is a unit vector, $c(t_0)$ is the tracer content at $t = 0$, τ_{die} is the time the material remains in the die, \mathfrak{R} and M are matrices which describe the leakage flows, the index μ is the number of time steps in one-screw rotation, the index n accounts for the amount of screw revolutions and $c(t_n + \tau_{die})$ is the concentration at the outlet of the extruder after a certain time.

VALIDATION OF THE MODEL

RTD measurements during the gelatinisation of starch

In order to check the model, residence-time experiments were performed using starch in a counter rotat-

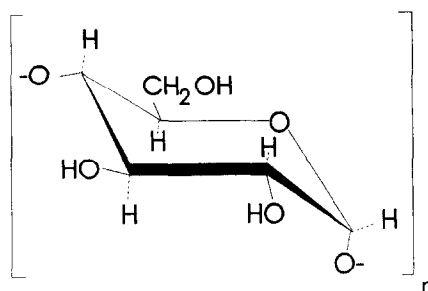


Fig. 7. α -D-glucopyranose.

ing twin screw extruder. Native starch consists of granules, containing two different polymers; amylose and amylopectine. Both polymers consist of α -D-glucopyranose elements (AGU = anhydroglucose-units) (Fig. 7). The difference between both polymers is that amylose is a nearly linear chain of about 2000 AGU and amylopectine is a branched chain of about 1 million AGU. Both molecules are ordered in such a way that crystallinity exists in the starch granule (Jenkins *et al.*, 1994). As the starch granules pass through the extruder, they will be disrupted due to several effects. Water will diffuse into a starch granule. The hydrogen bonds between the hydroxyl groups of an AGU and the residual water molecules in the starch will now be disrupted due to an increase in temperature. Successively amylose will diffuse out of the granule, due to the heat load and the shear in an extruder. Further shear and heat treatment will eventually disrupt the amylopectine entanglements and a complete starch gel is formed.

Experiments

During the experiments a counter-rotating closely intermeshing twin-screw extruder was used. This Pasquetti extruder had an L/D of 10 and a length of 40 cm. The potato-starch was delivered by AVEBE (Holland, Food grade, production year 1991).

The RTD was measured by a tracer technique. This technique is based on measuring atomic absorption spectrographs of the amount of Li in samples taken from the extrudate. A pulse of 0.4 g LiCl was added to the solid conveying zone of the extruder by using an injection system. Samples were taken at the die at regular time intervals. The samples were dried in a microwave oven and destructed by the use of nitric acid (p.a.) and sulphuric acid (p.a.) at a temperature increasing from 120 to 230°C. A clear solution was obtained after 3 h. Finally the amount of Li^+ ions in this solution were measured by Atomic Absorption Spectrometry (AAS type: Perkin-Elmer 1100 B). By using a reference line the AAS value can be correlated to the real Li^+ concentration. The error in this analysis is $< 1\%$. In Table 1 the extruder parameters used can be found. The fully filled length was measured using pressure transducers. The fully filled length expressed as the number of fully filled chambers can also

Table 1. Extruder settings during the experiments

No.	Pressure die (bar)	Pressure PI (bar)	Input starch (g min^{-1})	Input water (g min^{-1})	Input styrene (g min^{-1})	Screw rotations (RPM)	Perc. water (%)	Volume die (cm^3)
1	14	1	30	6.4	—	15	30	56.3
2	14	1	30	6.4	—	20	30	56.3
3	16	1	25.9	5.5	3	15	27	56.3
4	38	1	26.7	5	4	15	25	63.8
5	38	1	20	3	2.8	15	23	63.8
6	34	1	26.7	5	4	20	25	63.8
7	31	1	26.7	5	4	25	25	63.8
8	52	10	26.7	5	4	25	25	54.6

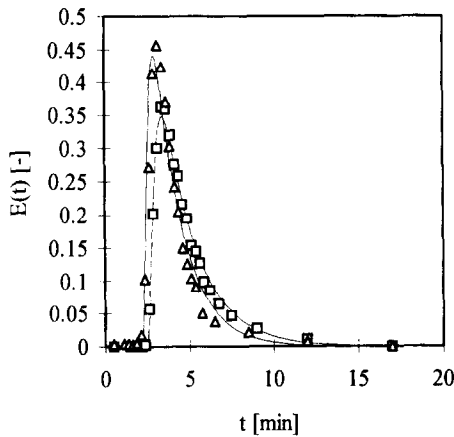


Fig. 8. Influence of the screw speed on the measured and modelled RTD curve during the gelatinization of starch: (---) model ($N = 15$ RPM, $v_f = 6$), (\square) measurements; (—) model ($N = 20$ RPM, $v_f = 4$), (\triangle) measurements.

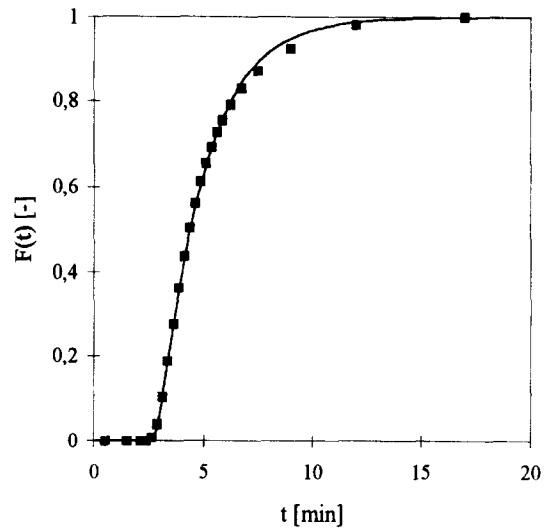


Fig. 9. Internal age distribution of experiment 1: (\blacksquare) measurements; (—) model.

be calculated:

$$v_f = \frac{P_{\text{die}}}{\Delta P} \quad (27)$$

where P_{die} is the die pressure and ΔP is the pressure drop between two consecutive chambers as calculated from the leakage flow equations. To check whether the data obtained by this method were correct, the extruder was stopped and the barrel removed. It appeared that the amount of fully filled chambers counted in this way, agreed in all cases with the amount of fully filled chambers as obtained by using equation 27.

Results and discussion

In Fig. 8 measured residence-time curves of the gelatinisation of starch in a twin screw extruder are compared with the curves as predicted by the model. The model needs as input parameters the screw speed, the throughput and the fully filled length only. In Fig. 9 the internal age function, $F(t)$, is set out for the modelled as well as for the measured data.

By making use of the first three moments of both curves the experimental data were correlated to the modelled curves. In Table 2 the three moments (the residence time, the variance and the skewness) of both these curves, as given by the model and as calculated from the measurements, are given. Although the moments, as calculated by the model, have a tendency to be somewhat lower than those as obtained from the measurements, the agreement is generally good, considering the fact that the model uses no adjustable parameters. Parameters calculated by the model, like the amount of leakage flows and the density in the different zones, are given in Table 3.

Trends as predicted by the model were calculated and plotted in the Figs 10–12. Only one parameter was varied at the time. In Fig. 10 an increase of the screw speed results in a diminishing decrease of the residence time. The variance and the skewness of the curve increase slightly due to the screw speed dependency of the leakage flow. This effect seems logical because [eq. (4)] at an increase of the screw speed the leakage flows increase, resulting in a larger distribution in residence time, while the breakthrough

Table 2. Moments measured and calculated for the different experiments performed

Experimental number	Measurements			Model		
	\bar{t} (min)	σ (min)	χ (min)	\bar{t} (min)	σ (min)	χ (min)
1	5.1	2.4	2.9	4.98 (97%)	2.04 (86%)	2.50 (86%)
2	4.4	2.3	3.1	4.18 (94%)	1.63 (71%)	1.98 (64%)
3	5.9	2.2	2.9	6.20 (95%)	2.45 (91%)	2.93 (97%)
4	6.4	2.8	3.4	6.16 (96%)	2.35 (84%)	2.83 (82%)
5	7.9	2.5	2.7	7.96 (100%)	3.03 (84%)	3.35 (79%)
6	5.4	2.0	2.6	5.41 (99%)	1.99 (99%)	2.31 (88%)
7	4.9	2.1	2.7	4.91 (99%)	1.79 (85%)	1.98 (74%)
8	6.1	3.0	3.5	6.22 (98%)	2.82 (94%)	2.98 (86%)

Table 3. Different parameters as calculated by the model

Experimental number	1	2	3	4	5	6	7	8
Fully filled chambers	6	4	4	5	6	5	5	10
t_d (s)	150	132	197	168	252	180	160	160
t_{die} (s)	118	108	165	168	220	156	141	141
$Q_{leak,pff}$ (cm ³ s ⁻¹)	0.56	0.56	0.54	0.56	0.40	0.56	0.56	0.56
$Q_{leak,ff}$ (cm ³ s ⁻¹)	5.5	7.5	5.7	5.6	5.7	7.6	9.6	9.6
Q_{th} (cm ³ s ⁻¹)	6.0	8.0	6.0	6.0	6.0	8.0	10.0	10.0
Q_{in} (cm ³ s ⁻¹)	0.47	0.47	0.45	0.47	0.34	0.47	0.47	0.47
Q_{out} (cm ³ s ⁻¹)	0.48	0.52	0.34	0.38	0.29	0.41	0.45	0.39
ρ_0 (10 ³ kg m ⁻³)	1.29	1.29	1.26	1.26	1.28	1.26	1.26	1.26
ρ_{graft} (10 ³ kg m ⁻³)	1.3	1.2	1.7	1.6	1.5	1.5	1.3	1.5
$\Delta p/\eta$ (s ⁻¹)	194.2	268.7	205.8	202.5	210.2	278.3	352.8	358.4
degree of fill (—)	0.078	0.059	0.075	0.078	0.056	0.059	0.047	0.047
α (—)	0.171	0.128	0.165	0.171	0.122	0.128	0.102	0.102
(—)								

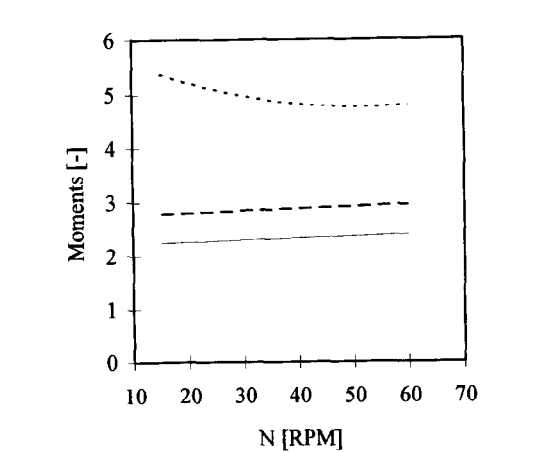


Fig. 10. Calculated moments vs the screw speed (constant throughput); (—) skewness (min³); (— · —) variance (min²); (····) residence time (min).

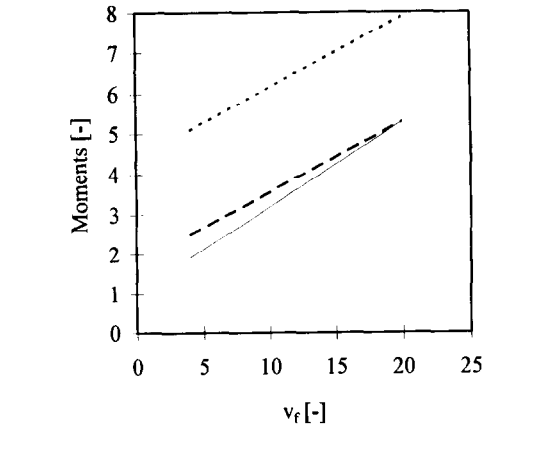


Fig. 11. Calculated moments vs the amount of filled chambers (all other parameters remained constant). (—) Skewness (min³); (— · —) variance (min²); (····) residence time (min).

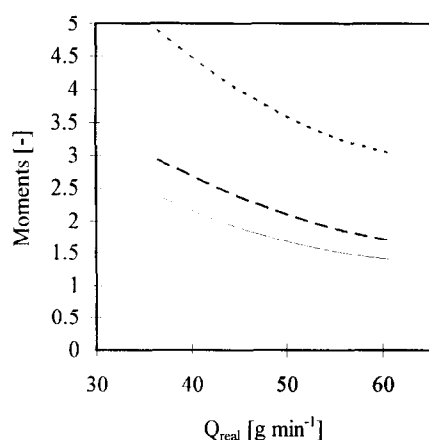


Fig. 12. Calculated moments vs the throughput (all other parameters remained constant). (—) Skewness (min^3); (---) variance (min^2); (- - -) residence time (min).

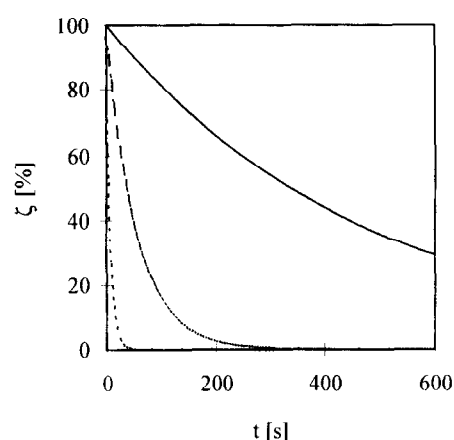


Fig. 13. Decay of $\text{K}_2\text{S}_2\text{O}_8$ at several reaction temperatures. (—) $T = 383 \text{ K}$; (---) $T = 403 \text{ K}$; (- - -) $T = 423 \text{ K}$.

time of material decreases. Increasing the amount of fully filled chambers (Fig. 11) results in a linear increase of the residence time. The second and the third moment also increase due to the increase of the leakage flows. Increasing the throughput (Fig. 12) results in decreasing values for the three moments, which is logical when eq. (5) is examined.

RTD measurements during reactive extrusion

Beside RTD measurements performed during the gelatinisation of starch also RTD measurements were performed during the reaction of styrene with starch forming polystyrene-grafted-starch.

The polymerisation of styrene is a free radical addition polymerisation (Fanta *et al.*, 1987). This implies that the polymer chains are formed in a very short time, after which they are excluded from further reaction. Every single polymer chain is initiated and terminated at different points in time. The reaction rate constants show an Arrhenius dependence of the following form (Brandrup, *et al.*, 1989, Rasmussen *et al.*, 1983, Bartlett and Nozaki, 1948, Yamada, *et al.*, 1991):

$$k_{j,x} = k_{j,x} e^{(-E_{a,j}/RT)} \quad (28)$$

The activation energy $E_{a,j} = 140.2 \text{ kJ mol}^{-1}$ and the frequency factor $k_{j,x} = 2.7 \times 10^{16} \text{ s}^{-1}$ (Henrici-Olivé, 1969). The copolymerisation and grafting was initiated using the thermal initiator $\text{K}_2\text{S}_2\text{O}_8$. Figure 13 gives the half-time decay of the initiator at different temperatures used.

Assuming that both the stationary-state hypothesis and the long chain hypothesis are valid the following final reaction rate equation can be written:

$$-R_M \cong k_p \left[\frac{k_d}{k_t} \right]^{1/2} c_I^{1/2} c_M \quad (29)$$

A radical starting a polymer chain can be formed due to the reaction of $\text{S}_2\text{O}_8^{2-}$ with the styrene monomer but also by radical formation on a starch chain. Due

to the very low solubility of styrene (Hefer, 1989) in a highly viscous starch gel it is assumed that graft copolymerisation only takes place if a radical formed on the starch is situated on the boundary layer between the starch gel and the styrene phase.

For homopolymerisation of styrene, k_p and k_t are given by Brandrup *et al.* (1989) and Yamada *et al.* (1991). These values are the results of several studies. Theoretically, eq. (29) gives the polymerization rate at every stage in the reaction. However, in practice deviations from this equation can occur in a concentrated system, better known as the Trommsdorff effect or gel effect. The gel effect results in both higher molecular weights and higher conversions than would be expected from conventional kinetics. It should be noted that already at 30% conversion the gel effects become measurable (Yamada *et al.*, 1991). As can be seen from the reaction scheme (Fig. 14, Jarowenko, 1969), three products occur: homopolymer polystyrene, grafted starch and virgin starch.

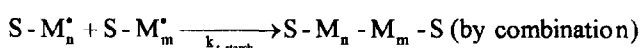
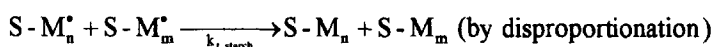
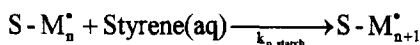
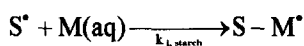
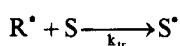
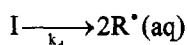
Reactive extrusion experiments

The styrene and the initiator were delivered by Merck. The extruder was fed with a composition of 73 wt% native starch, 0.5 wt% initiator, 18 wt% water and 8.5 wt% styrene. The native starch contained already 15 wt% water. Table 1 presents the extruder parameters tested.

Results and discussion

In Fig. 15 the model is compared with the measurements of the gelatinised starch with and without reaction. In both cases the total throughput, the screw speed and the temperature profile were equal. It can clearly be seen that the breakthrough time of the starch/styrene mixture has increased. This effect can not solely be declared by the decrease of filled volume. By re-examining the model and taking the density of the processed material into account the breakthrough time of the measured curve could be predicted again.

Reactions in the styrene - starch phase :



Reactions in the styrene phase :

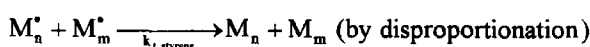
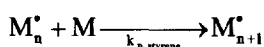
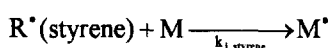


Fig. 14. Graft copolymerisation scheme of styrene to starch (I = initiator, R = initiator radical, M = styrene monomer, S = starch backbone).

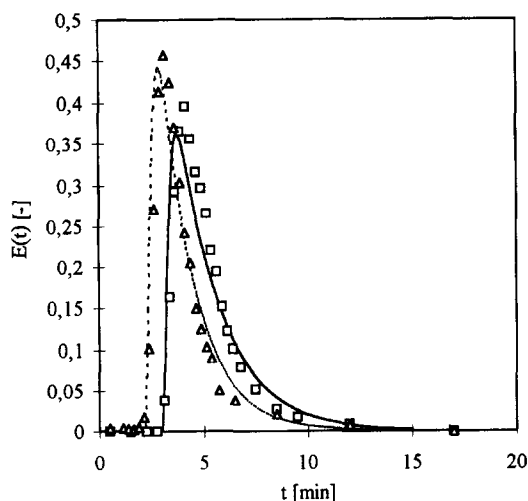


Fig. 15. Influence on the RTD of the grafting reaction of styrene on starch: (—) model, (□) measurements (reaction); (---) model, (△) measurements (no reaction).

These calculated results were compared with the density measurements of the grafted material and gelatinised starch. At 25°C and atmospheric pressure the density appeared to be $1.5 \times 10^3 \text{ kg/m}^3$. This value is high compared to that of normal gelatinised starch, which has a density of $1.3 \times 10^3 \text{ kg/m}^3$. The reason that the model could predict such a distribution

Table 4. Initial extruder settings

Screw speed	15	(RPM)
Fully filled length	5	
Throughput	35	(g min ⁻¹)

change is because it calculates the density related parameter $\Delta p/\eta$ from the following formula:

$$\frac{\Delta p}{\eta} = \frac{Q_{\text{leak, ff}} - AN}{B} = \frac{4NV_c - Q_{\text{out}} - AN}{B} \quad (30)$$

By taking this parameter, the breakthrough time and the amount of fully filled chambers into account the density in the fully filled zone and the die can be calculated. By comparing the curves in Fig. 16 it can be seen that an increase of the screw speed, at constant throughput, results in a decrease of the residence time. Increase of the amount of fully filled chambers (Fig. 17) results in the expected increase of the first three moments. Also the decrease of the throughput (Fig. 18) results in an increase of the first three moments as expected.

CONCLUSIONS

Starch extrusion with and without reaction is a complex operation. Beside extruder parameters like screw rotation, filled length and throughput also material properties like the viscosity and density are very

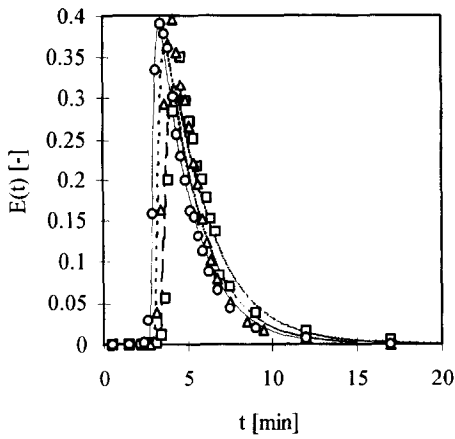


Fig. 16. Influence of the screw speed on the measured and modelled RTD curve during reaction (constant throughput): (---) model ($N = 25$ RPM), (\circ) measurements; (----) model ($N = 20$ RPM), (Δ) measurements; (—) model ($N = 15$ RPM), (\square) Measurements.

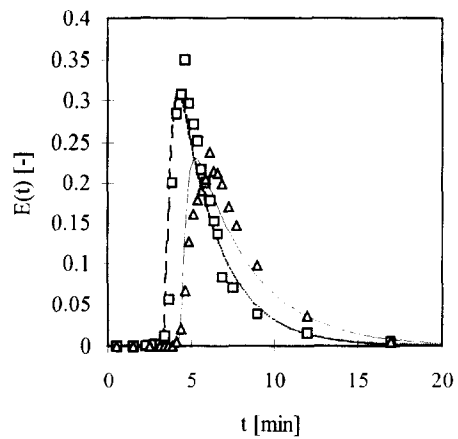


Fig. 18. Influence of the throughput on the measured and modelled RTD curve during reaction: (---) model ($Q_r = 25.8$ g min⁻¹), (Δ) measurements; (----) model ($Q_r = 35.7$ g min⁻¹), (\square) measurements.

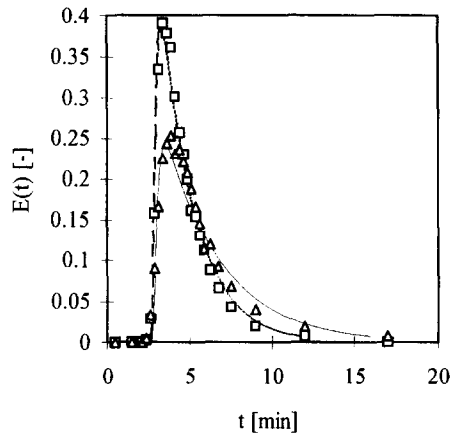


Fig. 17. Influence of the amount of filled chambers on the measured and modelled RTD during reaction: (---) model ($v_f = 5$), (\square) measurements; (----) model ($v_f = 10$), (Δ) measurements.

important in the whole process. By performing RTD measurements and using the model as described in this paper, direct conclusions about important parameters like the filled length, the hold-up and whether the reactive extrusion process is sensitive to density changes can be obtained. In this way no viscosity or density measurements have to be done and the extruder needs not to be opened to determine the filled length.

Beside these results also the following conclusions can be drawn:

- It is possible to set-up a RTD model of the form: $C_{out}(t) = (\mathfrak{R} M^n) C_{in}(t)$. Here \mathfrak{R} and M are matrices describing the influence of the extruder parameters (like screw rotation, screw geometry ect.).

- Without any adjustable parameters this model is able to describe the RTD curve of starch being processed in an extruder with good results.
- When during reactive extrusion a material property like the density changes rapidly, the model needs an extra parameter (the breakthrough time) to take this effect into account.
- An increase of the rotation rate causes a decrease of the residence time while the variance and the skewness stay more the less the same.
- Increasing the fully filled length causes an increase of the residence time, the variance and the skewness.
- Decreasing the throughput causes an increase of the residence time but a decrease of the variance and the skewness.

Acknowledgement

This investigation was carried out with support of the Dutch National Innovation Oriented Program Carbohydrates (IOP-k).

NOTATION

$A_{t,f,s,c}$	geometric constants, m ³
$B_{t,f,s,c}$	geometric constants, m ³
c_0	input concentration, kg m ⁻³
$c_{1...v}$	concentration in the screw chambers, kg m ⁻³
c_{bl}	concentration in the boundary layer, kg m ⁻³
c_d	concentration in the die zone, kg m ⁻³
c_h	concentration in the hopper zone, kg m ⁻³
c_s	average concentration in the last four screw chamber, kg m ⁻³
d	thickness boundary layer, m
E_a	activation energy, J mol ⁻¹
$E(t)$	exit age distribution, dimensionless
$F(t)$	internal age distribution, dimensionless
k	reaction rate constant, s ⁻¹

m	amount of screws, dimensionless
$MO()$	moments of the nonnormalised curve
M	transfer matrix
n	time index, indicating the amount of steps taken in one screw revolution, dimensionless
N	screw rotations, s^{-1}
Δp	pressure difference between two consecutive, Pa chambers in fully filled zone
Q_{pc}	leakage flow through calendar gap, $m^3 s^{-1}$
Q_{pf}	leakage flow through flight gap, $m^3 s^{-1}$
Q_{in}	input flow in a zone, $m^3 s^{-1}$
Q_{out}	output flow in a zone, $m^3 s^{-1}$
Q_{leak}	leakage flow in a zone, $m^3 s^{-1}$
Q_{ps}	leakage flow through side gap, $m^3 s^{-1}$
Q_{real}	real throughput, $m^3 s^{-1}$
Q_t	leakage flow through tetrahedron gap, $m^3 s^{-1}$
$Q_{th, zone}$	theoretical flow in a zone, $m^3 s^{-1}$
$Q_{out, zone}$	output flow in a zone, $m^3 s^{-1}$
Q_{out}	throughput extruder, $m^3 s^{-1}$
R	transfer matrix
t_d	residence time in the die, s
V_c	volume C-shaped chamber m^3
V_{bl}	volume barrier layer, m^3
V_{ic}	volume input chambers, m^3
V_h	volume hopper zone, m^3
V_{pf}	volume partially filled chambers, m^3
V_{die}	volume die, m^3
t_n	time steps with index n , s
t_i	time steps with index i , s

Greek letters

α	degree of fill in not fully filled zone, dimensionless
η	viscosity in a chamber, Pa s
μ	interval dimensionless
μ	amount of steps in a revolution, dimensionless
v	amount of chambers on the screw, dimensionless
ρ_0	density input flow, $kg m^{-3}$
ρ_{graft}	density graft copolymer, $kg m^{-3}$
τ_{die}	mean residence time die, s
χ	skewness, min^3

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